

PATENT ABSTRACTS OF JAPAN

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(54) METHOD FOR MANUFACTURING SOLAR BATTERY MODULE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for manufacturing a solar battery module that has improved adhesion strength with a front cover or a back one.

SOLUTION: In this method for manufacturing a solar battery module having a basic lamination structure of front cover/solar battery element/back cover, an ethylene unsaturated silane compound modification olefin resin sheet that is an olefin resin modified by an ethylene unsaturated silane compound expressed by a following expression (I) $R_1SiR_2nY_{3-n}$, has a radical generator content of 0.001 wt.% or less, and a gel fraction of 30% or less is included at least between the front cover and the solar battery element for fusion and lamination. In the expression (I), R1, R2, Y, and (n) indicate an ethylene unsaturated hydrocarbon group or a hydrocarbon oxy group, a hydrocarbon group, an organic group that can be subjected to hydrolysis, and an integer of 0-2, respectively.

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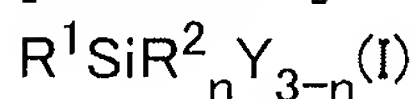
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CLAIMS

[Claim(s)]

[Claim 1]It sets to manufacture a solar cell module of a basic laminated structure of a front cover / solar battery element / back cover, It is the olefin system resin which denaturalized at least with an ethylene nature unsaturation silane compound expressed with following general formula (I) between a front cover and a solar battery element, A manufacturing method of a solar cell module which content of a radical generator is 0.001 or less % of the weight, and is characterized by a gel fraction's making 30% or less of ethylene nature unsaturation silane compound denaturation olefin system resin sheet intervene, and carrying out weld lamination.

[Formula 1]



[As for R^1 , an ethylene nature unsaturation hydrocarbon group or a hydrocarbon oxy group shows the organic group which can be hydrolyzed among formula (I), a hydrocarbon group and Y show R^2 , and n is an integer of 0-2.]

[Claim 2]A manufacturing method of the solar cell module according to claim 1 which makes said ethylene nature unsaturation silane compound denaturation olefin system resin sheet intervene also between a solar battery element and a back cover, and carries out weld lamination.

[Claim 3]A manufacturing method of the solar cell module according to claim 1 or 2 whose content of an ethylene nature unsaturation silane compound unit in ethylene nature unsaturation silane compound denaturation olefin system resin is 0.1 to 10 % of the weight.

[Claim 4]A manufacturing method of the solar cell module according to any one of claims 1 to 3 whose front cover is glass and whose back cover is fluorine system resin.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of the solar cell module which is excellent in adhesive strength with a front cover or a back cover in more detail about the manufacturing method of the solar cell module which used semiconductors, such as an amorphous silicon.

[0002]

[Description of the Prior Art]From before, the solar cell module using semiconductors, such as an amorphous silicon, The sealing agent sheet by transparent resin etc. is made to be placed between the acceptance surface sides of the solar battery element, Make a sealing agent sheet same as the above not intervene at the rear-face side, or the front cover which is from transparent substrates, such as glass aiming at protection, on the acceptance surface side is made to intervene, the back cover which consists of resin, metal or glass aiming at moisture proof, etc. is provided, respectively, and it is manufactured by carrying out weld lamination.

[0003]And although ethylene-vinylacetate copolymer resin is mainly used from a field, such as excelling in transparency or dampproofing and excelling in the fusion processing nature at the time of lamination as the sealing agent sheet, It cannot say that adhesive strength with a front cover or a back cover is not necessarily enough, but the weak point is inherent in the problem of ***** at the time of long-term use on the outdoors.

[0004]On the other hand, that crosslinking reaction is made to occur to sealing agent resin, and the intensity of the material itself, heat resistance, endurance, etc. should be given to it at the time of weld lamination to JP,62-14111,B. The method of using for ethylene-vinylacetate copolymer resin the resin sheet which added a silane coupling agent and organic peroxide again to JP,62-9232,B. The method of using the resin sheet which added organic peroxide for the ethylene-vinylacetate copolymer resin which carried out graft denaturation with the organic silane compound again to JP,6-104729,B. Although the method of using for ethylene-ethylenic-unsaturated-carboxylic-acid ester ethylene nature unsaturation silane compound ternary polymerization object resin the resin sheet which added organic peroxide is proposed, respectively, Since all are making organic peroxide contain, organic peroxide decomposes at the time of those sheet forming, and the crosslinking reaction of resin is caused, The actual condition is that have a fault, such as sheet forming becoming difficult or the fusion processing nature at the time of lamination falling, or the decomposition product of organic peroxide origin remaining in an adhesion interface, and causing adhesion inhibition at the time of lamination, and the further improvement is still called for.

[0005]

[Problem(s) to be Solved by the Invention]This invention was made in view of the above-mentioned conventional technology, and it aims at providing the manufacturing method of the solar cell module this invention excels [solar cell module] in adhesive strength with a front cover or a back cover.

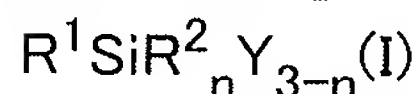
[0006]

[Means for Solving the Problem]This invention is set to manufacture a solar cell module of a

basic laminated structure of a front cover / solar battery element / back cover, It is the olefin system resin which denaturalized at least with an ethylene nature unsaturation silane compound expressed with following general formula (I) between a front cover and a solar battery element, Content of a radical generator is 0.001 or less % of the weight, and a gel fraction makes a gist a manufacturing method of a solar cell module which makes 30% or less of ethylene nature unsaturation silane compound denaturation olefin system resin sheet intervene, and carries out weld lamination.

[0007]

[Formula 2]



[0008][As for R^1 , an ethylene nature unsaturation hydrocarbon group or a hydrocarbon oxy group shows the organic group which can be hydrolyzed among formula (I), a hydrocarbon group and Y show R^2 , and n is an integer of 0-2.]

[0009]

[Embodiment of the Invention]In the manufacturing method of the solar cell module of the basic laminated structure of a front cover / solar battery element / back cover of this invention, Although the material in which all are more publicly known than before is used, respectively, the laminated material which sandwiched with glass etc. as a front cover, sandwiched with the silicon semiconductor etc. as a solar battery element, and sandwiched metal, such as resin, such as a fluorine system polymer, and aluminum, by resin as a back cover, or glass, As a front cover, glass is preferred for fluorine system resin as a back cover again.

[0010]In this invention, polyvinyl fluoride resin, polyvinylidene fluoride resin, ethylene-tetrafluoroethylene copolymer resin, etc. are preferred as a fluorine system polymer as a back cover.

[0011]And in the manufacturing method of the solar cell module of this invention, It is the olefin system resin which denaturalized at least with the ethylene nature unsaturation silane compound expressed with said general formula (I) between said front cover and said solar battery element, The content of a radical generator is 0.001 or less % of the weight, and it is indispensable that a gel fraction makes 30% or less of ethylene nature unsaturation silane compound denaturation olefin system resin sheet intervene, and carries out weld lamination.

[0012]Here as R^1 in said general formula (I) as the ethylene nature unsaturation silane compound, For example, a propenyl group, a butenyl group, a cyclohexenyl group, gamma-(meta) acryloyloxypropyl group, etc. as R^2 , For example, a methyl group, an ethyl group, a propyl group, a decyl group, a phenyl group, etc. as Y, For example, a methoxy group, an ethoxy basis, a formyloxy group, an acetoxy group, They are mentioned by a propionyloxy group, an alkylamino group, arylamino group, etc., respectively, and as an example of such an ethylene nature unsaturation silane compound, For example, vinyltrimetoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane, gamma-methacryloyl oxypropyl trimethoxysilane, etc. are mentioned.

[0013]As ethylene nature unsaturation silane compound denaturation olefin system resin in this invention, Olefin system resin to this resin 100 weight section under existence of radical generators, such as organic peroxide of about 0.01-5 weight sections, with said about 0.1-5 weight sections of ethylene nature unsaturation silane compounds. For example, the denaturation olefin system resin produced by carrying out melt kneading at the temperature more than the decomposition temperature of a radical generator using an extrusion machine etc., and giving a grafting reaction process, Or further 90 to 99.99 % of the weight of ethylene, and said 10 to 0.01 % of the weight of ethylene nature unsaturation silane compounds by a case, for example with vinyl acetate, acrylic acid (meta), acrylic ester (meta), etc. Materials more publicly known than before as ethylene nature unsaturation silane compound denaturation olefin system resin, such as denaturation ethylene resin produced by making carry out radical copolymerization under the usual high voltage radical polymerization condition, can be used.

[0014]As olefin system resin of the former ethylene nature unsaturation silane compound denaturation olefin system resin, The homopolymer of with a carbon numbers [, such as

ethylene, propylene, and 1-butene,] of about two to eight alpha olefin, Those alpha olefins and ethylene, propylene, 1-butene, a 3-methyl-1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, They are mentioned by the copolymer with other with a carbon numbers [, such as 1-decene,] of about two to 20 alpha olefins, vinyl acetate, acrylic acid (meta), acrylic ester (meta), etc., etc., and specifically, For example, ethylene homopolymers, such as low, inside, and high density polyethylene (branched state or straight chain shape), Ethylene propylene rubber, an ethylene-1-butene copolymer, an ethylene-4-methyl-1-pentene copolymer, An ethylene-1-hexene copolymer, an ethylene-1-octene copolymer, An ethylene-vinylacetate copolymer, an ethylene-(meta) acrylic acid copolymer, Propylene resin, such as ethylene resin, such as an ethylene-(meta) ethyl acrylate copolymer, a propylene homopolymer, a propylene-ethylenic copolymer, and a propylene-ethylene-1-butene copolymer, and 1-butene homopolymer, 1-butene system resin, such as 1-butene-ethylenic copolymer and 1-butene-propylene copolymer, etc. are mentioned. In this invention, ethylene resin is preferred in inside.

[0015]As a radical generator used in the grafting reaction process of the former ethylene nature unsaturation silane compound denaturation olefin system resin, For example, hydroperoxides, such as diisopropylbenzene hydronalium peroxide and 2,5-dimethyl- 2,5-JI (hydronalium peroxy) hexane, Di-t-butyl peroxide, t-butyl cumyl peroxide, Dicumyl peroxide, 2,5-dimethyl- 2,5-di-tert-butyl peroxide hexane, The dialkyl peroxide of 2,5-dimethyl- 2,5-di-tert-butyl peroxide hexyne-3 grade, The bis- 3 and 5, 5-trimethylhexanoyl peroxide, octanoyl peroxide, Benzoyl peroxide, o-methylbenzoyl peroxide, Diacyl peroxide, such as 2,4-dichlorobenzyl peroxide, T-butyl peroxyacetate, t-butylperoxy-2-ethylhexanoate, T-butylperoxy perpivalate, t-butyl peroxyoctoate, t-butylperoxyisopropylcarbonate, t-butyl peroxybenzoate, di-t-butyl diperoxyphthalate, 2,5-dimethyl- 2,5-JI (benzoylperoxy) hexane, The peroxy ester species of 2,5-dimethyl- 2,5-JI (benzoylperoxy) hexyne-3 grade, Azo compounds, such as organic peroxide, such as ketone peroxides, such as methyl ethyl ketone peroxide and cyclohexanon peroxide, azobisisobutyronitrile, and azobis (2,4-dimethylvaleronitrile), etc. are mentioned.

[0016]In the manufacturing method of the solar cell module of this invention, as said ethylene nature unsaturation silane compound denaturation olefin system resin as a sealing agent sheet made to intervene between said front cover and said solar battery element at least, That whose content of an ethylene nature unsaturation silane compound unit is 0.1 to 10 % of the weight is preferred, and especially the thing that is 0.5 to 5 % of the weight is preferred. The content of an ethylene nature unsaturation silane compound unit serves as the tendency for improvement of adhesive strength with a front cover or a back cover to be hard to accept, in said less than range, and, on the other hand, it becomes the tendency for crosslinking reaction to occur easily at the time of sheet forming, by said excess of the range.

[0017]Said ethylene nature unsaturation silane compound denaturation olefin system resin has that preferred whose melt flow rates in 190 ** are 0.01-200g/10 minutes from fields, such as sheet forming nature and an adhesive property, and especially its thing that are 0.1-100g/10 minutes is preferred. That fields, such as fusion processing nature, to whose melting point is 120 ** or less is preferred.

[0018]And as said ethylene nature unsaturation silane compound denaturation olefin system resin as a sealing agent sheet which is made to intervene between said front cover and said solar battery element at least, and can be set in this invention to carry out weld lamination, It is indispensable that the content of a radical generator is 0.001 or less % of the weight, and a gel fraction is 30% or less. The content of a radical generator in said excess of the range. At the time of lamination, the decomposition product of radical generator origin remains in an adhesion interface, adhesion inhibition is caused, and in said excess of the range, the fusion processing nature at the time of lamination will fall [a gel fraction], and, as for all, improvement of adhesive strength with a front cover or a back cover will be accepted.

[0019]As said ethylene nature unsaturation silane compound denaturation olefin system resin as a sealing agent sheet which can be set here to carry out weld lamination, It may be the dilution by native olefin system resin of said denaturation olefin system resin, In that case, let each of said ethylene nature unsaturation silane compound unit content, said melt flow rate, said melting point, said radical generators and free radical content, and said gel fractions be the things as

dilution.

[0020] Said ethylene nature unsaturation silane compound denaturation olefin system resin in this invention, Usually, are resin which is contacted for moisture under existence of a silanol condensation catalyst and which can make the structure of cross linkage form in resin with what is called a water cross-linking method, and also as a sealing agent sheet in this invention, Although excessive arch forming should be avoided from fields, such as fusion processing nature, and it is necessary to consider it as 30% or less like the above-mentioned as a gel fraction at the time of lamination, it is preferred to form the structure of cross linkage after lamination, and it is preferred that it is not less than 60% as the gel fraction.

[0021] The crosslinking treatment by the water cross-linking method, for example Dibutyltin diacetate, Dibutyl tin JIRAUTETO, dibutyl tin JIOKUTETO, dioctyl tin JIRAUTETO, etc., Beforehand the silanol condensation catalyst which promotes the dehydrating condensation reaction between the silanols of silicone to said denaturation olefin system resin. the ** which is blended about 0.001-10 weight sections, and is used to this resin 100 weight section, or is not used -- ordinary temperature -- about 200 **, although usually made about [ordinary temperature -100 **] liquefied or by making steam-like water usually contact 10 seconds -- about one week covering about 1 minute -1 day, The laminating process etc. which do not establish the process of such water crosslinking treatment uniquely, but ** also mentions later especially can attain the gel fraction in the sealing agent sheet after the lamination in this invention.

[0022] To said ethylene nature unsaturation silane compound denaturation olefin system resin in this invention. In the range which is not spoiled, the effect of this invention Thermoplastics and rubbers other than said ethylene nature unsaturation silane compound denaturation olefin system resin, And an antioxidant, light stabilizer, an ultraviolet ray absorbent, a nucleating agent, a neutralizer, a spray for preventing static electricity, lubricant, an antiblocking agent, a dispersing agent, a fluidity improving agent, a plasticizer, a release agent, fire retardant, colorant, a filler, etc. may be added.

[0023] Said ethylene nature unsaturation silane compound denaturation olefin system resin sheet in this invention, In accordance with the sheet forming method of usual thermoplastics, it is fabricated at the temperature of about 100-250 ** by the extrusion machine provided with the T die, and is fabricated by a thickness of about 0.1-1.0 mm melt extruding and by carrying out cooling solidification.

[0024] Manufacture of the solar cell module of this invention makes said denaturation olefin system resin sheet intervene between said front cover and said solar battery element at least, In this order, pile up a front cover / denaturation olefin system resin sheet / solar battery element / back cover, and preferably, Said denaturation olefin system resin sheet is made to intervene also between said solar battery element and said back cover, a front cover / denaturation olefin system resin sheet / solar battery element / denaturation olefin system resin sheet / back cover being piled up in this order, or, A front cover / denaturation olefin system resin sheet / solar battery element / denaturation olefin system resin, and a back cover laminated material sheet are piled up in this order, It is a temperature higher than the melting point of denaturation olefin system resin, and a desirable temperature higher not less than 10 ** than the melting point, and about 20-200 kPa is usually preferably made by carrying out weld lamination under the application of pressure of about 30-150 kPa the time for about 5 to 30 minutes about 1 to 60 minutes.

[0025]

[Example] Hereafter, although an example explains this invention still more concretely, this invention is not limited to the following examples, unless the gist is exceeded.

[0026] Example 1 density 0.910 g/cm³, the melt flow rate 3.5g in 190 **/straight-chain-shape ethylene-1-octene copolymer 100 weight section for 10 minutes, The amount part of vinyltrimetoxysilane duplexs, and dicumyl peroxide 0.06 weight section, After supplying the screw diameter of 40 mm, and the 1 axis extrusion machine of ratio-of-length-to-diameter25, carrying out melt kneading at 220 **, after carrying out a dry blend for 2 minutes, and giving a grafting

reaction process, to strand shape melt extruding and by pelletizing, The pellet of the vinyltrimetoxysilane denaturation straight-chain-shape ethylene-1-octene copolymer (it is displayed as "the Silang graft LLDPE" among the following table.) was obtained. The obtained denaturation thing is 112 ** in melting point for 1.5 % of the weight of content of a vinyltrimetoxysilane unit, and the melt flow rate 2g in 190 **/10 minutes.

The content which extracted unreacted dicumyl peroxide with methanol and analyzed it using the gas chromatograph was 0.001 or less % of the weight.

[0027]This vinyltrimetoxysilane denaturation straight-chain-shape ethylene-1-octene copolymer, The 0.6-mm-thick denaturation olefin system resin sheet was fabricated with the die temperature of 150 ** melt extruding and by cooling to the sheet shaped from the extrusion machine of screw diameter [of 65 mm], and ratio-of-length-to-diameter26 provided with the 1000-mm-wide T die. Although this sheet forming was performed over 5 hours, the moldability in the meantime was stable. The gel fraction was measured by the method shown below, and the result was shown in Table 1.

Weight % of the insoluble matter after carrying out a Soxhlet extraction in the gel fraction xylene boiling point for 10 hours was measured.

[0028]It piles up in order of blue plate glass / denaturation olefin system resin sheet / solar battery element / denaturation olefin system resin sheet / poly fluoridation vinyl sheet ("TEDORA" by U.S. Du Pont) using the obtained sheet, After carrying out weld lamination on condition of the temperature shown in Table 1 under the pressure of 58kPa, and time, by cooling rationally, About the solar cell module obtained by manufacturing a solar cell module. About each between blue plate glass and a denaturation olefin system resin sheet and between a poly fluoridation vinyl sheet (it is displayed as "PVF" among the following table.), and a denaturation olefin system resin sheet, when visual observation of the adhesion state was carried out, having pasted all up uniformly was checked. Peel strength was measured by the method shown below, and the gel fraction of the denaturation olefin system resin sheet after exfoliation was measured by the same method as the above, and each result was shown in Table 1.

The peel strength by 90-degree exfoliation was measured by a part for speed-of-testing/of 100 mm using the sample cut off to peel strength the width of 10 mm.

[0029]20 % of the weight of example diacetic acid vinyl unit content, the melt flow rate 15g in 190 **/ethylene-vinylacetate copolymer 97 weight section for 10 minutes, 15 % of the weight of vinyl acetate unit content, the melt flow rate 2g in 190 **/ethylene-vinylacetate copolymer 3 weight section for 10 minutes, The amount part of vinyltrimetoxysilane duplexs, and t-butylperoxy2-ethylhexanoate 0.3 weight section, After supplying the screw diameter of 40 mm, and the 1 axis extrusion machine of ratio-of-length-to-diameter25, carrying out melt kneading at 190 **, after carrying out a dry blend for 2 minutes, and giving a grafting reaction process, to strand shape melt extruding and by pelletizing, The pellet of the vinyltrimetoxysilane denaturation ethylene-vinylacetate copolymer (it is displayed as "Silang graft EVA" among the following table.) was obtained. The obtained denaturation thing is 89 ** in melting point for 1.3 % of the weight of content of a vinyltrimetoxysilane unit, and the melt flow rate 9g in 190 **/10 minutes. The content which extracted unreacted t-butylperoxy2-ethylhexanoate with methanol, and was analyzed using the gas chromatograph was 0.001 or less % of the weight.

[0030]The moldability was stable when the outside which used the obtained vinyltrimetoxysilane denaturation ethylene-vinylacetate copolymer fabricated the denaturation olefin system resin sheet like Example 1. The gel fraction in a sheet was measured and the result was shown in Table 1. When the solar cell module was manufactured and visual observation of the adhesion state was carried out by carrying out weld lamination about each between blue plate glass and a denaturation olefin system resin sheet and between a poly fluoridation vinyl sheet and a denaturation olefin system resin sheet, having pasted all up uniformly was checked. Peel strength was measured, further, the gel fraction of the denaturation olefin system resin sheet after exfoliation was measured, and each result was shown in Table 1.

[0031]19 % of the weight of example 3 ethyl-acrylate unit content, the melt flow rate 5g in 190

*/ethylene-ethyl acrylate copolymer 100 weight section for 10 minutes, Vinyltrimetoxysilane 2.5 weight section and t-butylperoxy2-ethylhexanoate 0.3 weight section, After supplying the screw diameter of 40 mm, and the 1 axis extrusion machine of ratio-of-length-to-diameter25, carrying out melt kneading at 190 **, after carrying out a dry blend for 2 minutes, and giving a grafting reaction process, to strand shape melt extruding and by pelletizing, The pellet of the vinyltrimetoxysilane denaturation ethylene-ethyl acrylate copolymer (it is displayed as "the Silang graft EEA" among the following table.) was obtained. The obtained denaturation thing is 90 ** in melting point for 1.4 % of the weight of content of a vinyltrimetoxysilane unit, and the melt flow rate 4.5g in 190 **/10 minutes.

The content which extracted unreacted t-butylperoxy2-ethylhexanoate with methanol, and was analyzed using the gas chromatograph was 0.001 or less % of the weight.

[0032]The moldability was stable when the outside which used the obtained vinyltrimetoxysilane denaturation ethylene-ethyl acrylate copolymer fabricated the denaturation olefin system resin sheet like Example 1. The gel fraction in a sheet was measured and the result was shown in Table 1. When the solar cell module was manufactured and visual observation of the adhesion state was carried out by carrying out weld lamination about each between blue plate glass and a denaturation olefin system resin sheet and between a poly fluoridation vinyl sheet and a denaturation olefin system resin sheet, having pasted all up uniformly was checked. Peel strength was measured, further, the gel fraction of the denaturation olefin system resin sheet after exfoliation was measured, and each result was shown in Table 1.

[0033]To a reactor with an agitator with example 4 content volume of 1.5 l., ethylene, gamma-methacryloyl oxypropyl trimethoxysilane, And by supplying continuously the mixture of methyl acrylate, and t-butylperoxy neodecanoate, and carrying out copolymerization with polymerization pressure 200MPa and the polymerization temperature of 190 **, The pellet of the ethylene-gamma-methacryloyl-oxypropyl-trimethoxysilane methyl acrylate ternary polymerization object (it is displayed as "the Silang copolymerization LDPE" among the following table.) was obtained. The obtained denaturation thing is 81 ** in melting point for 1.1 % of the weight of content of gamma-methacryloyl-oxypropyl-trimethoxysilane unit, 25 % of the weight of content of a methyl acrylate unit, and the melt flow rate 10g in 190 **/10 minutes.

The content which extracted unreacted t-butylperoxy neodecanoate with methanol, and was analyzed using the gas chromatograph was 0.001 or less % of the weight.

[0034]The moldability was stable when the outside which used the obtained ethylene-gamma-methacryloyl-oxypropyl-trimethoxysilane methyl acrylate copolymer fabricated the denaturation olefin system resin sheet like Example 1. The gel fraction in a sheet was measured and the result was shown in Table 1. When the solar cell module was manufactured and visual observation of the adhesion state was carried out by carrying out weld lamination about each between blue plate glass and a denaturation olefin system resin sheet and between a poly fluoridation vinyl sheet and a denaturation olefin system resin sheet, having pasted all up uniformly was checked. Peel strength was measured, further, the gel fraction of the denaturation olefin system resin sheet after exfoliation was measured, and each result was shown in Table 1.

[0035]The outside which added and used the amount part of dicumyl peroxide duplexs for vinyltrimetoxysilane denaturation ethylene-vinylacetate copolymer 100 weight section obtained in comparative example 1 Example 2, Like Example 1, when the denaturation olefin system resin sheet was fabricated, crosslinking reaction occurred in the handle part in 15 minutes after a shaping start, and sheet forming became difficult. The gel fraction was measured about the sheet when shaping is good, and the result was shown in Table 1. A solar cell module is manufactured by carrying out weld lamination using a sheet when shaping is good, About each between blue plate glass and a denaturation olefin system resin sheet and between a poly fluoridation vinyl sheet and a denaturation olefin system resin sheet. When visual observation of the adhesion state was carried out, many air bubbles expected to depend all on the decomposition product of a radical generator were accepted, and many portions which have not been pasted up existed. Peel strength was measured, further, the gel fraction of the denaturation olefin system resin

sheet after exfoliation was measured, and each result was shown in Table 1.

[0036] 19 % of the weight of comparative example 2 ethyl-acrylate unit content, the melt flow rate 5g/10 minutes in 190 **, To ethylene-ethyl acrylate copolymer 100 weight section with a melting point of 90 **. The outside which added and used gamma-methacryloyl-oxypropyl-trimethoxysilane 1.5 weight section and di-t-butyl peroxide 1 weight section, Like Example 1, when the denaturation olefin system resin (it is displayed as "Silang graft EEA" among following table.) sheet was fabricated, crosslinking reaction occurred in the handle part in 20 minutes after a shaping start, and sheet forming became difficult. The gel fraction was measured about the sheet when shaping is good, and the result was shown in Table 1. A solar cell module is manufactured by carrying out weld lamination using a sheet when shaping is good, About each between blue plate glass and a denaturation olefin system resin sheet and between a poly fluoridation vinyl sheet and a denaturation olefin system resin sheet. When visual observation of the adhesion state was carried out, many air bubbles expected to depend all on the decomposition product of a radical generator were accepted, and many portions which have not been pasted up existed. Peel strength was measured, further, the gel fraction of the denaturation olefin system resin sheet after exfoliation was measured, and each result was shown in Table 1.

[0037]

[Table 1]

表 1

	変性オレフィン系樹脂シート			積層条件		モジュール製造後の樹脂シート		
	樹脂種類	ラジカル発生 剤含有量 (重量%)	ゲル分率 (%)	温度 (℃)	時間 (分)	ゲル分率 (%)	接着強度 (N/10mm)	
							対ガラス	対PVF
実施例 1	シラングラフト LLDPE	≤0.001	2	130 150	30 15	73 80	21 35	15 30
実施例 2	シラングラフト EVA	≤0.001	5	130 150	30 15	71 74	28 43	24 39
実施例 3	シラングラフト EBA	≤0.001	3	130 150	30 15	75 76	25 41	22 39
実施例 4	シラン 共重合 LDPE	≤0.001	5	130 150	30 15	82 84	33 52	26 41
比較例 1	シラングラフト EVA	1.65	14	130 150	30 15	47 82	10 48	4 45
比較例 2	シラングラフト EBA	0.92	11	130 150	30 15	53 85	12 50	5 46

[0038]

[Effect of the Invention] According to this invention, the manufacturing method of the solar cell module which is excellent in adhesive strength with a front cover or a back cover can be provided.

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TECHNICAL FIELD

[Field of the Invention]This invention relates to the manufacturing method of the solar cell module which is excellent in adhesive strength with a front cover or a back cover in more detail about the manufacturing method of the solar cell module which used semiconductors, such as an amorphous silicon.

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PRIOR ART

[Description of the Prior Art]From before, the solar cell module using semiconductors, such as an amorphous silicon, The sealing agent sheet by transparent resin etc. is made to be placed between the acceptance surface sides of the solar battery element, Make a sealing agent sheet same as the above not intervene at the rear-face side, or the front cover which is from transparent substrates, such as glass aiming at protection, on the acceptance surface side is made to intervene, the back cover which consists of resin, metal or glass aiming at moisture proof, etc. is provided, respectively, and it is manufactured by carrying out weld lamination.

[0003]And although ethylene-vinylacetate copolymer resin is mainly used from a field, such as excelling in transparency or dampproofing and excelling in the fusion processing nature at the time of lamination as the sealing agent sheet, It cannot say that adhesive strength with a front cover or a back cover is not necessarily enough, but the weak point is inherent in the problem of ***** at the time of long-term use on the outdoors.

[0004]On the other hand, that crosslinking reaction is made to occur to sealing agent resin, and the intensity of the material itself, heat resistance, endurance, etc. should be given to it at the time of weld lamination to JP,62-14111,B. The method of using for ethylene-vinylacetate copolymer resin the resin sheet which added a silane coupling agent and organic peroxide again to JP,62-9232,B. The method of using the resin sheet which added organic peroxide for the ethylene-vinylacetate copolymer resin which carried out graft denaturation with the organic silane compound again to JP,6-104729,B. Although the method of using for ethylene-ethylenic-unsaturated-carboxylic-acid ester ethylene nature unsaturation silane compound ternary polymerization object resin the resin sheet which added organic peroxide is proposed, respectively, Since all are making organic peroxide contain, organic peroxide decomposes at the time of those sheet forming, and the crosslinking reaction of resin is caused, The actual condition is that have a fault, such as sheet forming becoming difficult or the fusion processing nature at the time of lamination falling, or the decomposition product of organic peroxide origin remaining in an adhesion interface, and causing adhesion inhibition at the time of lamination, and the further improvement is still called for.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention]According to this invention, the manufacturing method of the solar cell module which is excellent in adhesive strength with a front cover or a back cover can be provided.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]This invention was made in view of the above-mentioned conventional technology, and it aims at providing the manufacturing method of the solar cell module this invention excels [solar cell module] in adhesive strength with a front cover or a back cover.

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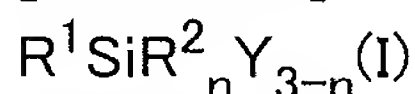
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MEANS

[Means for Solving the Problem]This invention is set to manufacture a solar cell module of a basic laminated structure of a front cover / solar battery element / back cover, It is the olefin system resin which denaturalized at least with an ethylene nature unsaturation silane compound expressed with following general formula (I) between a front cover and a solar battery element, Content of a radical generator is 0.001 or less % of the weight, and a gel fraction makes a gist a manufacturing method of a solar cell module which makes 30% or less of ethylene nature unsaturation silane compound denaturation olefin system resin sheet intervene, and carries out weld lamination.

[0007]

[Formula 2]



[0008][As for R^1 , an ethylene nature unsaturation hydrocarbon group or a hydrocarbon oxy group shows the organic group which can be hydrolyzed among formula (I), a hydrocarbon group and Y show R^2 , and n is an integer of 0-2.]

[0009]

[Embodiment of the Invention]In the manufacturing method of the solar cell module of the basic laminated structure of a front cover / solar battery element / back cover of this invention, Although the material in which all are more publicly known than before is used, respectively, the laminated material which sandwiched with glass etc. as a front cover, sandwiched with the silicon semiconductor etc. as a solar battery element, and sandwiched metal, such as resin, such as a fluorine system polymer, and aluminum, by resin as a back cover, or glass, As a front cover, glass is preferred for fluorine system resin as a back cover again.

[0010]In this invention, polyvinyl fluoride resin, polyvinylidene fluoride resin, ethylene-tetrafluoroethylene copolymer resin, etc. are preferred as a fluorine system polymer as a back cover.

[0011]And in the manufacturing method of the solar cell module of this invention, It is the olefin system resin which denaturalized at least with the ethylene nature unsaturation silane compound expressed with said general formula (I) between said front cover and said solar battery element, The content of a radical generator is 0.001 or less % of the weight, and it is indispensable that a gel fraction makes 30% or less of ethylene nature unsaturation silane compound denaturation olefin system resin sheet intervene, and carries out weld lamination.

[0012]Here as R^1 in said general formula (I) as the ethylene nature unsaturation silane compound, For example, a propenyl group, a butenyl group, a cyclohexenyl group, gamma-(meta) acryloyloxypropyl group, etc. as R^2 , For example, a methyl group, an ethyl group, a propyl group, a decyl group, a phenyl group, etc. as Y, For example, a methoxy group, an ethoxy basis, a formyloxy group, an acetoxo group, They are mentioned by a propionyloxy group, an alkylamino group, arylamino group, etc., respectively, and as an example of such an ethylene nature unsaturation silane compound, For example, vinyltrimetoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane, gamma-methacryloyl oxypropyl trimethoxysilane, etc. are mentioned.

[0013]As ethylene nature unsaturation silane compound denaturation olefin system resin in this

invention, Olefin system resin to this resin 100 weight section under existence of radical generators, such as organic peroxide of about 0.01-5 weight sections, with said about 0.1-5 weight sections of ethylene nature unsaturation silane compounds. For example, the denaturation olefin system resin produced by carrying out melt kneading at the temperature more than the decomposition temperature of a radical generator using an extrusion machine etc., and giving a grafting reaction process, Or further 90 to 99.99 % of the weight of ethylene, and said 10 to 0.01 % of the weight of ethylene nature unsaturation silane compounds by a case, for example with vinyl acetate, acrylic acid (meta), acrylic ester (meta), etc. Materials more publicly known than before as ethylene nature unsaturation silane compound denaturation olefin system resin, such as denaturation ethylene resin produced by making carry out radical copolymerization under the usual high voltage radical polymerization condition, can be used.

[0014]As olefin system resin of the former ethylene nature unsaturation silane compound denaturation olefin system resin, The homopolymer of with a carbon numbers [, such as ethylene, propylene, and 1-butene,] of about two to eight alpha olefin, Those alpha olefins and ethylene, propylene, 1-butene, a 3-methyl-1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, They are mentioned by the copolymer with other with a carbon numbers [, such as 1-decene,] of about two to 20 alpha olefins, vinyl acetate, acrylic acid (meta), acrylic ester (meta), etc., etc., and specifically, For example, ethylene homopolymers, such as low, inside, and high density polyethylene (branched state or straight chain shape), Ethylene propylene rubber, an ethylene-1-butene copolymer, an ethylene-4-methyl-1-pentene copolymer, An ethylene-1-hexene copolymer, an ethylene-1-octene copolymer, An ethylene-vinylacetate copolymer, an ethylene-(meta) acrylic acid copolymer, Propylene resin, such as ethylene resin, such as an ethylene-(meta) ethyl acrylate copolymer, a propylene homopolymer, a propylene-ethylenic copolymer, and a propylene-ethylene-1-butene copolymer, and 1-butene homopolymer, 1-butene system resin, such as 1-butene-ethylenic copolymer and 1-butene-propylene copolymer, etc. are mentioned. In this invention, ethylene resin is preferred in inside.

[0015]As a radical generator used in the grafting reaction process of the former ethylene nature unsaturation silane compound denaturation olefin system resin, For example, hydroperoxides, such as diisopropylbenzene hydronalium peroxide and 2,5-dimethyl- 2,5-JI (hydronalium peroxy) hexane, Di-t-butyl peroxide, t-butyl cumyl peroxide, Dicumyl peroxide, 2,5-dimethyl- 2,5-di-tert-butyl peroxide hexane, The dialkyl peroxide of 2,5-dimethyl- 2,5-di-tert-butyl peroxide hexyne-3 grade, The bis- 3 and 5, 5-trimethylhexanoyl peroxide, octanoyl peroxide, Benzoyl peroxide, o-methylbenzoyl peroxide, Diacyl peroxide, such as 2,4-dichlorobenzyl peroxide, T-butyl peroxyacetate, t-butylperoxy-2-ethylhexanoate, T-butylperoxy perpivalate, t-butyl peroxyoctoate, t-butylperoxyisopropylcarbonate, t-butyl peroxybenzoate, di-t-butyl diperoxyphthalate, 2,5-dimethyl- 2,5-JI (benzoylperoxy) hexane, The peroxy ester species of 2,5-dimethyl- 2,5-JI (benzoylperoxy) hexyne-3 grade, Azo compounds, such as organic peroxide, such as ketone peroxides, such as methyl ethyl ketone peroxide and cyclohexanon peroxide, azobisisobutyronitrile, and azobis (2,4-dimethylvaleronitrile), etc. are mentioned.

[0016]In the manufacturing method of the solar cell module of this invention, as said ethylene nature unsaturation silane compound denaturation olefin system resin as a sealing agent sheet made to intervene between said front cover and said solar battery element at least, That whose content of an ethylene nature unsaturation silane compound unit is 0.1 to 10 % of the weight is preferred, and especially the thing that is 0.5 to 5 % of the weight is preferred. The content of an ethylene nature unsaturation silane compound unit serves as the tendency for improvement of adhesive strength with a front cover or a back cover to be hard to accept, in said less than range, and, on the other hand, it becomes the tendency for crosslinking reaction to occur easily at the time of sheet forming, by said excess of the range.

[0017]Said ethylene nature unsaturation silane compound denaturation olefin system resin has that preferred whose melt flow rates in 190 ** are 0.01-200g/10 minutes from fields, such as sheet forming nature and an adhesive property, and especially its thing that are 0.1-100g/10 minutes is preferred. That fields, such as fusion processing nature, to whose melting point is 120 ** or less is preferred.

[0018]And as said ethylene nature unsaturation silane compound denaturation olefin system

resin as a sealing agent sheet which is made to intervene between said front cover and said solar battery element at least, and can be set in this invention to carry out weld lamination, It is indispensable that the content of a radical generator is 0.001 or less % of the weight, and a gel fraction is 30% or less. The content of a radical generator in said excess of the range. At the time of lamination, the decomposition product of radical generator origin remains in an adhesion interface, adhesion inhibition is caused, and in said excess of the range, the fusion processing nature at the time of lamination will fall [a gel fraction], and, as for all, improvement of adhesive strength with a front cover or a back cover will be accepted.

[0019]As said ethylene nature unsaturation silane compound denaturation olefin system resin as a sealing agent sheet which can be set here to carry out weld lamination, It may be the dilution by native olefin system resin of said denaturation olefin system resin, In that case, let each of said ethylene nature unsaturation silane compound unit content, said melt flow rate, said melting point, said radical generators and free radical content, and said gel fractions be the things as dilution.

[0020]Said ethylene nature unsaturation silane compound denaturation olefin system resin in this invention, Usually, are resin which is contacted for moisture under existence of a silanol condensation catalyst and which can make the structure of cross linkage form in resin with what is called a water cross-linking method, and also as a sealing agent sheet in this invention, Although excessive arch forming should be avoided from fields, such as fusion processing nature, and it is necessary to consider it as 30% or less like the above-mentioned as a gel fraction at the time of lamination, it is preferred to form the structure of cross linkage after lamination, and it is preferred that it is not less than 60% as the gel fraction.

[0021]The crosslinking treatment by the water cross-linking method, for example Dibutyltin diacetate, Dibutyl tin JIRAUTETO, dibutyl tin JIOKUTETO, dioctyl tin JIRAUTETO, etc., Beforehand the silanol condensation catalyst which promotes the dehydrating condensation reaction between the silanols of silicone to said denaturation olefin system resin. the ** which is blended about 0.001-10 weight sections, and is used to this resin 100 weight section, or is not used -- ordinary temperature - about 200 **, although usually made about [ordinary temperature -100 **] liquefied or by making steam-like water usually contact 10 seconds - about one week covering about 1 minute -1 day, The laminating process etc. which do not establish the process of such water crosslinking treatment uniquely, but ** also mentions later especially can attain the gel fraction in the sealing agent sheet after the lamination in this invention.

[0022]To said ethylene nature unsaturation silane compound denaturation olefin system resin in this invention. In the range which is not spoiled, the effect of this invention Thermoplastics and rubbers other than said ethylene nature unsaturation silane compound denaturation olefin system resin, And an antioxidant, light stabilizer, an ultraviolet ray absorbent, a nucleating agent, a neutralizer, a spray for preventing static electricity, lubricant, an antiblocking agent, a dispersing agent, a fluidity improving agent, a plasticizer, a release agent, fire retardant, colorant, a filler, etc. may be added.

[0023]Said ethylene nature unsaturation silane compound denaturation olefin system resin sheet in this invention, In accordance with the sheet forming method of usual thermoplastics, it is fabricated at the temperature of about 100-250 ** by the extrusion machine provided with the T die, and is fabricated by a thickness of about 0.1-1.0 mm melt extruding and by carrying out cooling solidification.

[0024]Manufacture of the solar cell module of this invention makes said denaturation olefin system resin sheet intervene between said front cover and said solar battery element at least, In this order, pile up a front cover / denaturation olefin system resin sheet / solar battery element / back cover, and preferably, Said denaturation olefin system resin sheet is made to intervene also between said solar battery element and said back cover, a front cover / denaturation olefin system resin sheet / solar battery element / denaturation olefin system resin sheet / back cover being piled up in this order, or, A front cover / denaturation olefin system resin sheet / solar battery element / denaturation olefin system resin, and a back cover laminated material sheet are piled up in this order, It is a temperature higher than the melting

point of denaturation olefin system resin, and a desirable temperature higher not less than 10 ** than the melting point, and about 20-200 kPa is usually preferably made by carrying out weld lamination under the application of pressure of about 30-150 kPa the time for about 5 to 30 minutes about 1 to 60 minutes.

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EXAMPLE

[Example]Hereafter, although an example explains this invention still more concretely, this invention is not limited to the following examples, unless the gist is exceeded.

[0026]Example 1 density 0.910 g/cm^3 , the melt flow rate 3.5g in 190 **/straight-chain-shape ethylene-1-octene copolymer 100 weight section for 10 minutes, The amount part of vinyltrimetoxysilane duplexs, and dicumyl peroxide 0.06 weight section, After supplying the screw diameter of 40 mm, and the 1 axis extrusion machine of ratio-of-length-to-diameter25, carrying out melt kneading at 220 **, after carrying out a dry blend for 2 minutes, and giving a grafting reaction process, to strand shape melt extruding and by pelletizing, The pellet of the vinyltrimetoxysilane denaturation straight-chain-shape ethylene-1-octene copolymer (it is displayed as "the Silang graft LLDPE" among the following table.) was obtained. The obtained denaturation thing is 112 ** in melting point for 1.5 % of the weight of content of a vinyltrimetoxysilane unit, and the melt flow rate 2g in 190 **/10 minutes.

The content which extracted unreacted dicumyl peroxide with methanol and analyzed it using the gas chromatograph was 0.001 or less % of the weight.

[0027]This vinyltrimetoxysilane denaturation straight-chain-shape ethylene-1-octene copolymer, The 0.6-mm-thick denaturation olefin system resin sheet was fabricated with the die temperature of 150 ** melt extruding and by cooling to the sheet shaped from the extrusion machine of screw diameter [of 65 mm], and ratio-of-length-to-diameter26 provided with the 1000-mm-wide T die. Although this sheet forming was performed over 5 hours, the moldability in the meantime was stable. The gel fraction was measured by the method shown below, and the result was shown in Table 1.

Weight % of the insoluble matter after carrying out a Soxhlet extraction in the gel fraction xylene boiling point for 10 hours was measured.

[0028]It piles up in order of blue plate glass / denaturation olefin system resin sheet / solar battery element / denaturation olefin system resin sheet / poly fluoridation vinyl sheet ("TEDORA" by U.S. Du Pont) using the obtained sheet, After carrying out weld lamination on condition of the temperature shown in Table 1 under the pressure of 58kPa, and time, by cooling rationally, About the solar cell module obtained by manufacturing a solar cell module. About each between blue plate glass and a denaturation olefin system resin sheet and between a poly fluoridation vinyl sheet (it is displayed as "PVF" among the following table.), and a denaturation olefin system resin sheet, when visual observation of the adhesion state was carried out, having pasted all up uniformly was checked. Peel strength was measured by the method shown below, and the gel fraction of the denaturation olefin system resin sheet after exfoliation was measured by the same method as the above, and each result was shown in Table 1.

The peel strength by 90-degree exfoliation was measured by a part for speed-of-testing/of 100 mm using the sample cut off to peel strength the width of 10 mm.

[0029]20 % of the weight of example diacetic acid vinyl unit content, the melt flow rate 15g in 190 **/ethylene-vinylacetate copolymer 97 weight section for 10 minutes, 15 % of the weight of vinyl acetate unit content, the melt flow rate 2g in 190 **/ethylene-vinylacetate copolymer 3 weight section for 10 minutes, The amount part of vinyltrimetoxysilane duplexs, and t-

butylperoxy2-ethylhexanoate 0.3 weight section, After supplying the screw diameter of 40 mm, and the 1 axis extrusion machine of ratio-of-length-to-diameter25, carrying out melt kneading at 190 **, after carrying out a dry blend for 2 minutes, and giving a grafting reaction process, to strand shape melt extruding and by pelletizing, The pellet of the vinyltrimetoxysilane denaturation ethylene-vinylacetate copolymer (it is displayed as "Silang graft EVA" among the following table.) was obtained. The obtained denaturation thing is 89 ** in melting point for 1.3 % of the weight of content of a vinyltrimetoxysilane unit, and the melt flow rate 9g in 190 **/10 minutes. The content which extracted unreacted t-butylperoxy2-ethylhexanoate with methanol, and was analyzed using the gas chromatograph was 0.001 or less % of the weight.

[0030]The moldability was stable when the outside which used the obtained vinyltrimetoxysilane denaturation ethylene-vinylacetate copolymer fabricated the denaturation olefin system resin sheet like Example 1. The gel fraction in a sheet was measured and the result was shown in Table 1. When the solar cell module was manufactured and visual observation of the adhesion state was carried out by carrying out weld lamination about each between blue plate glass and a denaturation olefin system resin sheet and between a poly fluoridation vinyl sheet and a denaturation olefin system resin sheet, having pasted all up uniformly was checked. Peel strength was measured, further, the gel fraction of the denaturation olefin system resin sheet after exfoliation was measured, and each result was shown in Table 1.

[0031]19 % of the weight of example 3 ethyl-acrylate unit content, the melt flow rate 5g in 190 **/ethylene-ethyl acrylate copolymer 100 weight section for 10 minutes, Vinyltrimetoxysilane 2.5 weight section and t-butylperoxy2-ethylhexanoate 0.3 weight section, After supplying the screw diameter of 40 mm, and the 1 axis extrusion machine of ratio-of-length-to-diameter25, carrying out melt kneading at 190 **, after carrying out a dry blend for 2 minutes, and giving a grafting reaction process, to strand shape melt extruding and by pelletizing, The pellet of the vinyltrimetoxysilane denaturation ethylene-ethyl acrylate copolymer (it is displayed as "the Silang graft EEA" among the following table.) was obtained. The obtained denaturation thing is 90 ** in melting point for 1.4 % of the weight of content of a vinyltrimetoxysilane unit, and the melt flow rate 4.5g in 190 **/10 minutes.

The content which extracted unreacted t-butylperoxy2-ethylhexanoate with methanol, and was analyzed using the gas chromatograph was 0.001 or less % of the weight.

[0032]The moldability was stable when the outside which used the obtained vinyltrimetoxysilane denaturation ethylene-ethyl acrylate copolymer fabricated the denaturation olefin system resin sheet like Example 1. The gel fraction in a sheet was measured and the result was shown in Table 1. When the solar cell module was manufactured and visual observation of the adhesion state was carried out by carrying out weld lamination about each between blue plate glass and a denaturation olefin system resin sheet and between a poly fluoridation vinyl sheet and a denaturation olefin system resin sheet, having pasted all up uniformly was checked. Peel strength was measured, further, the gel fraction of the denaturation olefin system resin sheet after exfoliation was measured, and each result was shown in Table 1.

[0033]To a reactor with an agitator with example 4 content volume of 1.5 l., ethylene, gamma-methacryloyl oxypropyl trimethoxysilane, And by supplying continuously the mixture of methyl acrylate, and t-butylperoxy neodecanoate, and carrying out copolymerization with polymerization pressure 200MPa and the polymerization temperature of 190 **, The pellet of the ethylene-gamma-methacryloyl-oxypropyl-trimethoxysilane methyl acrylate ternary polymerization object (it is displayed as "the Silang copolymerization LDPE" among the following table.) was obtained. The obtained denaturation thing is 81 ** in melting point for 1.1 % of the weight of content of gamma-methacryloyl-oxypropyl-trimethoxysilane unit, 25 % of the weight of content of a methyl acrylate unit, and the melt flow rate 10g in 190 **/10 minutes.

The content which extracted unreacted t-butylperoxy neodecanoate with methanol, and was analyzed using the gas chromatograph was 0.001 or less % of the weight.

[0034]The moldability was stable when the outside which used the obtained ethylene-gamma-

methacryloyl-oxypropyl-trimethoxysilane methyl acrylate copolymer fabricated the denaturation olefin system resin sheet like Example 1. The gel fraction in a sheet was measured and the result was shown in Table 1. When the solar cell module was manufactured and visual observation of the adhesion state was carried out by carrying out weld lamination about each between blue plate glass and a denaturation olefin system resin sheet and between a poly fluoridation vinyl sheet and a denaturation olefin system resin sheet, having pasted all up uniformly was checked. Peel strength was measured, further, the gel fraction of the denaturation olefin system resin sheet after exfoliation was measured, and each result was shown in Table 1.

[0035]The outside which added and used the amount part of dicumyl peroxide duplex for vinyltrimetoxysilane denaturation ethylene-vinylacetate copolymer 100 weight section obtained in comparative example 1 Example 2, Like Example 1, when the denaturation olefin system resin sheet was fabricated, crosslinking reaction occurred in the handle part in 15 minutes after a shaping start, and sheet forming became difficult. The gel fraction was measured about the sheet when shaping is good, and the result was shown in Table 1. A solar cell module is manufactured by carrying out weld lamination using a sheet when shaping is good, About each between blue plate glass and a denaturation olefin system resin sheet and between a poly fluoridation vinyl sheet and a denaturation olefin system resin sheet. When visual observation of the adhesion state was carried out, many air bubbles expected to depend all on the decomposition product of a radical generator were accepted, and many portions which have not been pasted up existed. Peel strength was measured, further, the gel fraction of the denaturation olefin system resin sheet after exfoliation was measured, and each result was shown in Table 1.

[0036]19 % of the weight of comparative example 2 ethyl-acrylate unit content, the melt flow rate 5g/10 minutes in 190 **, To ethylene-ethyl acrylate copolymer 100 weight section with a melting point of 90 **. The outside which added and used gamma-methacryloyl-oxypropyl-trimethoxysilane 1.5 weight section and di-t-butyl peroxide 1 weight section, Like Example 1, when the denaturation olefin system resin (it is displayed as "Silang graft EEA" among following table.) sheet was fabricated, crosslinking reaction occurred in the handle part in 20 minutes after a shaping start, and sheet forming became difficult. The gel fraction was measured about the sheet when shaping is good, and the result was shown in Table 1. A solar cell module is manufactured by carrying out weld lamination using a sheet when shaping is good, About each between blue plate glass and a denaturation olefin system resin sheet and between a poly fluoridation vinyl sheet and a denaturation olefin system resin sheet. When visual observation of the adhesion state was carried out, many air bubbles expected to depend all on the decomposition product of a radical generator were accepted, and many portions which have not been pasted up existed. Peel strength was measured, further, the gel fraction of the denaturation olefin system resin sheet after exfoliation was measured, and each result was shown in Table 1.

[0037]

[Table 1]

表 1

	変性オレフィン系樹脂シート			積層条件		モジュール製造後の樹脂シート		
	樹脂種類	ラジカル発生 剤含有量 (重量%)	ゲル分率 (%)	温度 (℃)	時間 (分)	ゲル分率 (%)	接着強度 (N/10mm)	
							対ガラス	対PVF
実施例 1	シラングラフト LLDPE	≤ 0.001	2	130 150	30 15	73 80	21 35	15 30
実施例 2	シラングラフト EVA	≤ 0.001	5	130 150	30 15	71 74	28 43	24 39
実施例 3	シラングラフト EBA	≤ 0.001	3	130 150	30 15	75 76	25 41	22 39
実施例 4	シラン 共重合 LDPE	≤ 0.001	5	130 150	30 15	82 84	33 52	26 41
比較例 1	シラングラフト EVA	1.65	14	130 150	30 15	47 82	10 48	4 45
比較例 2	シラングラフト EBA	0.92	11	130 150	30 15	53 85	12 50	5 46

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(54)【発明の名称】 太陽電池モジュールの製造方法

(57)【要約】

【目的】 フロントカバー或いはバックカバーとの接着強度に優れる太陽電池モジュールの製造方法を提供する。

【構成】 フロントカバー／太陽電池素子／バックカバーの基本積層構造の太陽電池モジュールを製造するにおいて、少なくともフロントカバーと太陽電池素子との間に、下記一般式(Ⅰ)で表されるエチレン性不飽和シラン化合物により変性されたオレフィン系樹脂であって、ラジカル発生剤の含有量が0.001重量%以下であり、且つ、ゲル分率が30%以下のエチレン性不飽和シラン化合物変性オレフィン系樹脂シートを介在させて融着積層する太陽電池モジュールの製造方法。

【化1】

$$R^1-SiR^2_nY_{3-n} \quad (Ⅰ)$$

〔式(Ⅰ)中、 R^1 はエチレン性不飽和ハイドロカーボン基又はハイドロカーボンオキシ基、 R^2 はハイドロカーボン基、 Y は加水分解可能な有機基を示し、 n は0～2の整数である。〕

【特許請求の範囲】

【請求項1】 フロントカバー／太陽電池素子／バックカバーの基本積層構造の太陽電池モジュールを製造するにおいて、少なくともフロントカバーと太陽電池素子との間に、下記一般式（I）で表されるエチレン性不飽和シラン化合物により変性されたオレフィン系樹脂であって、ラジカル発生剤の含有量が0.001重量%以下であり、且つ、ゲル分率が30%以下のエチレン性不飽和シラン化合物変性オレフィン系樹脂シートを介在させて融着積層することを特徴とする太陽電池モジュールの製造方法。

【化1】



〔式（I）中、 R^1 はエチレン性不飽和 hidrocarbon 基又は hidrocarbon オキシ基、 R^2 は hidrocarbon 基、Yは加水分解可能な有機基を示し、nは0～2の整数である。〕

【請求項2】 太陽電池素子とバックカバーとの間にも、前記エチレン性不飽和シラン化合物変性オレフィン系樹脂シートを介在させて融着積層する請求項1に記載の太陽電池モジュールの製造方法。

【請求項3】 エチレン性不飽和シラン化合物変性オレフィン系樹脂におけるエチレン性不飽和シラン化合物単位の含有量が0.1～10重量%である請求項1又は2に記載の太陽電池モジュールの製造方法。

【請求項4】 フロントカバーがガラスであり、バックカバーが弗素系樹脂である請求項1乃至3のいずれかに記載の太陽電池モジュールの製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、アモルファスシリコン等の半導体を用いた太陽電池モジュールの製造方法に関し、更に詳しくは、フロントカバー或いはバックカバーとの接着強度に優れる太陽電池モジュールの製造方法に関する。

【0002】

【従来の技術】従来より、アモルファスシリコン等の半導体を用いた太陽電池モジュールは、その太陽電池素子の受光面側に透明性樹脂等による封止材シートを介在させ、その受光面側に保護を目的としたガラス等の透明基板からなるフロントカバーを、裏面側に同上の封止材シートを介在せずして或いは介在させて、防湿を目的とした樹脂や金属或いはガラス等からなるバックカバーをそれぞれ設けて、融着積層することにより製造されている。

【0003】そして、その封止材シートとしては、透明性や防湿性に優れ、又、積層時の融着加工性に優れる等の面からエチレン-酢酸ビニル共重合体樹脂が主に用いられているが、フロントカバー或いはバックカバーとの接着強度が必ずしも十分とは言えず、屋外での長期使用

時にその弱点が露れるという問題を内在するものであった。

【0004】これに対して、融着積層時に封止材樹脂に架橋反応を生起させて材料自体の強度、及び耐熱性や耐久性等を付与すべく、例えば、特公昭62-14111号公報には、エチレン-酢酸ビニル共重合体樹脂にシランカップリング剤及び有機過酸化物を添加した樹脂シートを用いる方法が、又、特公昭62-9232号公報には、有機シラン化合物でグラフト変性したエチレン-酢酸ビニル共重合体樹脂に有機過酸化物を添加した樹脂シートを用いる方法が、又、特公平6-104729号公報には、エチレン-エチレン性不飽和カルボン酸エステル-エチレン性不飽和シラン化合物三元共重合体樹脂に有機過酸化物を添加した樹脂シートを用いる方法が、それぞれ提案されているが、いずれも有機過酸化物を含有させていることから、それらのシート成形時において有機過酸化物が分解して樹脂の架橋反応を惹起し、シート成形が困難となったり、積層時の融着加工性が低下したり、或いは、積層時に有機過酸化物由来の分解生成物が接着界面に残存して接着阻害を引き起こす等の欠点を有し、依然として更なる改良が求められているのが現状である。

【0005】

【発明が解決しようとする課題】本発明は、前述の従来技術に鑑みてなされたもので、従って、本発明は、フロントカバー或いはバックカバーとの接着強度に優れる太陽電池モジュールの製造方法を提供することを目的とする。

【0006】

【課題を解決するための手段】本発明は、フロントカバー／太陽電池素子／バックカバーの基本積層構造の太陽電池モジュールを製造するにおいて、少なくともフロントカバーと太陽電池素子との間に、下記一般式（I）で表されるエチレン性不飽和シラン化合物により変性されたオレフィン系樹脂であって、ラジカル発生剤の含有量が0.001重量%以下であり、且つ、ゲル分率が30%以下のエチレン性不飽和シラン化合物変性オレフィン系樹脂シートを介在させて融着積層する太陽電池モジュールの製造方法、を要旨とする。

【0007】

【化2】



【0008】〔式（I）中、 R^1 はエチレン性不飽和 hidrocarbon 基又は hidrocarbon オキシ基、 R^2 は hidrocarbon 基、Yは加水分解可能な有機基を示し、nは0～2の整数である。〕

【0009】

【発明の実施の形態】本発明の、フロントカバー／太陽電池素子／バックカバーの基本積層構造の太陽電池モジュールの製造方法において、フロントカバーとしてはガ

ラス等、又、太陽電池素子としてはシリコン半導体等、又、バックカバーとしては弗素系重合体等の樹脂、アルミニウム等の金属を樹脂でサンドイッチした積層物、或いはガラス等、いずれも従来より公知の材料がそれぞれ用いられるが、フロントカバーとしてはガラスが、又、バックカバーとしては弗素系樹脂が好適である。

【0010】尚、本発明において、バックカバーとしての弗素系重合体としては、ポリ弗化ビニル樹脂、ポリ弗化ビニリデン樹脂、エチレン-テトラフルオロエチレン共重合体樹脂等が好ましい。

【0011】そして、本発明の太陽電池モジュールの製造方法においては、少なくとも前記フロントカバーと前記太陽電池素子との間に、前記一般式(I)で表されるエチレン性不飽和シラン化合物により変性されたオレフィン系樹脂であって、ラジカル発生剤の含有量が0.001重量%以下であり、且つ、ゲル分率が30%以下のエチレン性不飽和シラン化合物変性オレフィン系樹脂シートを介在させて融着積層することが必須である。

【0012】ここで、そのエチレン性不飽和シラン化合物としての前記一般式(I)における R^1 としては、例えば、プロペニル基、ブテニル基、シクロヘキセニル基、 γ -(メタ)アクリロイルオキシプロピル基等が、 R^2 としては、例えば、メチル基、エチル基、プロピル基、デシル基、フェニル基等が、Yとしては、例えば、メトキシ基、エトキシ基、ホルミルオキシ基、アセトキシ基、プロピオニルオキシ基、アルキルアミノ基、アリールアミノ基等が、それぞれ挙げられ、このようなエチレン性不飽和シラン化合物の具体例としては、例えば、ビニルトリメトキシシラン、ビニルトリエトキシシラン、ビニルトリアセトキシシラン、 γ -メタクリロイルオキシプロピルトリメトキシシラン等が挙げられる。

【0013】本発明におけるエチレン性不飽和シラン化合物変性オレフィン系樹脂としては、オレフィン系樹脂を、該樹脂100重量部に対して0.01~5重量部程度の有機過氧化物等のラジカル発生剤の存在下に前記エチレン性不飽和シラン化合物0.1~5重量部程度と共に、例えば押出機等を用いてラジカル発生剤の分解温度以上の温度で熔融混練してグラフト反応工程に付して得られた変性オレフィン系樹脂、又は、例えばエチレン90~99.99重量%と前記エチレン性不飽和シラン化合物10~0.01重量%とを、場合により更に、酢酸ビニル、(メタ)アクリル酸、(メタ)アクリル酸エステル等と共に、通常の高圧ラジカル重合条件下にラジカル共重合させて得られた変性エチレン系樹脂等、従来よりエチレン性不飽和シラン化合物変性オレフィン系樹脂として公知の材料を用いることができる。

【0014】尚、前者のエチレン性不飽和シラン化合物変性オレフィン系樹脂のオレフィン系樹脂としては、エチレン、プロピレン、1-ブテン等の炭素数2~8程度の α -オレフィンの単独重合体、それらの α -オレフィ

ンとエチレン、プロピレン、1-ブテン、3-メチル-1-ブテン、1-ペンテン、4-メチル-1-ペンテン、1-ヘキセン、1-オクテン、1-デセン等の炭素数2~20程度の他の α -オレフィンや、酢酸ビニル、(メタ)アクリル酸、(メタ)アクリル酸エステル等との共重合体等が挙げられ、具体的には、例えば、低・中・高密度ポリエチレン等(分岐状又は直鎖状)のエチレン単独重合体、エチレン-プロピレン共重合体、エチレン-1-ブテン共重合体、エチレン-4-メチル-1-ペンテン共重合体、エチレン-1-ヘキセン共重合体、エチレン-1-オクテン共重合体、エチレン-酢酸ビニル共重合体、エチレン-(メタ)アクリル酸共重合体、エチレン-(メタ)アクリル酸エチル共重合体等のエチレン系樹脂、プロピレン単独重合体、プロピレン-エチレン共重合体、プロピレン-エチレン-1-ブテン共重合体等のプロピレン系樹脂、及び、1-ブテン単独重合体、1-ブテン-エチレン共重合体、1-ブテン-プロピレン共重合体等の1-ブテン系樹脂等が挙げられる。中で、本発明においては、エチレン系樹脂が好ましい。

【0015】又、前者のエチレン性不飽和シラン化合物変性オレフィン系樹脂のグラフト反応工程において用いられるラジカル発生剤としては、例えば、ジイソプロピルベンゼンヒドロパーオキシド、2,5-ジメチル-2,5-ジ(ヒドロパーオキシ)ヘキサン等のヒドロパーオキシド類、ジ- α -ブチルパーオキシド、 α -ブチルクロミルパーオキシド、ジクロミルパーオキシド、2,5-ジメチル-2,5-ジ(α -ブチルパーオキシ)ヘキサン、2,5-ジメチル-2,5-ジ(α -ブチルパーオキシ)ヘキシン-3等のジアルキルパーオキシド類、ビス-3,5,5-トリメチルヘキサノイルパーオキシド、オクタノイルパーオキシド、ベンゾイルパーオキシド、 α -メチルベンゾイルパーオキシド、2,4-ジクロロベンゾイルパーオキシド等のジアシルパーオキシド類、 α -ブチルパーオキシアセテート、 α -ブチルパーオキシ-2-エチルヘキサノエート、 α -ブチルパーオキシピバレート、 α -ブチルパーオキシオクトエート、 α -ブチルパーオキシイソプロピルカーボネート、 α -ブチルパーオキシベンゾエート、ジ- α -ブチルジパーオキシフタレート、2,5-ジメチル-2,5-ジ(ベンゾイルパーオキシ)ヘキサン、2,5-ジメチル-2,5-ジ(ベンゾイルパーオキシ)ヘキシン-3等のパーオキシエステル類、メチルエチルケトンパーオキシド、シクロヘキサノンパーオキシド等のケトンパーオキシド類等の有機過氧化物、アゾビスイソブチロニトリル、アゾビス(2,4-ジメチルバレロニトリル)等のアゾ化合物等が挙げられる。

【0016】本発明の太陽電池モジュールの製造方法において、少なくとも前記フロントカバーと前記太陽電池素子との間に介在させる封止材シートとしての前記エチ

レン性不飽和シラン化合物変性オレフィン系樹脂としては、エチレン性不飽和シラン化合物単位の含有量が0.1~10重量%であるものが好ましく、0.5~5重量%であるものが特に好ましい。エチレン性不飽和シラン化合物単位の含有量が前記範囲未満では、フロントカバー或いはバックカバーとの接着強度の改良が認められ難い傾向となり、一方、前記範囲超過では、シート成形時に架橋反応が生じ易い傾向となる。

【0017】又、前記エチレン性不飽和シラン化合物変性オレフィン系樹脂は、シート成形性、接着性等の面から、190℃でのメルトフローレートが0.01~200g/10分であるものが好ましく、0.1~100g/10分であるものが特に好ましい。又、融着加工性等の面から、融点が120℃以下であるものが好ましい。

【0018】そして、本発明において、少なくとも前記フロントカバーと前記太陽電池素子との間に介在させて融着積層するにおける封止材シートとしての前記エチレン性不飽和シラン化合物変性オレフィン系樹脂としては、ラジカル発生剤の含有量が0.001重量%以下であり、且つ、ゲル分率が30%以下であることが必須である。ラジカル発生剤の含有量が前記範囲超過では、積層時にラジカル発生剤由来の分解生成物が接着界面に残存して接着阻害を引き起こし、又、ゲル分率が前記範囲超過では、積層時の融着加工性が低下し、いずれも、フロントカバー或いはバックカバーとの接着強度の改良が認められないこととなる。

【0019】尚、ここで、融着積層するにおける封止材シートとしての前記エチレン性不飽和シラン化合物変性オレフィン系樹脂としては、前記変性オレフィン系樹脂の未変性オレフィン系樹脂による希釈物であってもよく、その場合、前記エチレン性不飽和シラン化合物単位含有量、前記メルトフローレート、前記融点、及び、前記ラジカル発生剤及び遊離基含有量、前記ゲル分率は、いずれも希釈物としてのものとする。

【0020】本発明における前記エチレン性不飽和シラン化合物変性オレフィン系樹脂は、通常、シラノール縮合触媒の存在下に水分と接触させる、所謂、水架橋法により樹脂内に架橋構造を形成させることができる樹脂であり、本発明における封止材シートとしても、積層時においては、融着加工性等の面から過度の架橋形成は避けるべきでありゲル分率として前述の如く30%以下とする必要があるが、積層後においては、架橋構造を形成しているのが好ましく、そのゲル分率として60%以上であるのが好ましい。

【0021】その水架橋法による架橋処理は、例えば、ジブチル錫ジアセテート、ジブチル錫ジラウテート、ジブチル錫ジオクテート、ジオクチル錫ジラウテート等の、シリコンのシラノール間の脱水縮合反応を促進するシラノール縮合触媒を予め前記変性オレフィン系樹脂に、該樹脂100重量部に対して0.001~10重量

部程度配合する等して用い、或いは用いずに、常温~200℃程度、通常は常温~100℃程度の液状又は蒸気状の水に10秒~1週間程度、通常は1分~1日程度にわたって接触させることによりなされるが、本発明における積層後の封止材シートにおけるゲル分率は、特にこのような水架橋処理の工程を独自に設けずとも、後述する積層工程等により達成することができる。

【0022】尚、本発明における前記エチレン性不飽和シラン化合物変性オレフィン系樹脂には、本発明の効果を損なわない範囲で、前記エチレン性不飽和シラン化合物変性オレフィン系樹脂以外の熱可塑性樹脂やゴム、及び、酸化防止剤、光安定剤、紫外線吸収剤、造核剤、中和剤、帯電防止剤、滑剤、ブロッキング防止剤、分散剤、流動性改良剤、可塑剤、離型剤、難燃剤、着色剤、充填材等が添加されてもよい。

【0023】本発明における前記エチレン性不飽和シラン化合物変性オレフィン系樹脂シートは、通常の熱可塑性樹脂のシート成形法に従い、例えば、Tダイを備えた押出機により、100~250℃程度の温度で熔融押出し、冷却固化させることにより、0.1~1.0mm程度の厚みで成形される。

【0024】本発明の太陽電池モジュールの製造は、少なくとも前記フロントカバーと前記太陽電池素子との間に前記変性オレフィン系樹脂シートを介在させて、フロントカバー/変性オレフィン系樹脂シート/太陽電池素子/バックカバーをこの順序で重ね合わせ、好ましくは、前記太陽電池素子と前記バックカバーとの間にも前記変性オレフィン系樹脂シートを介在させて、フロントカバー/変性オレフィン系樹脂シート/太陽電池素子/変性オレフィン系樹脂シート/バックカバーをこの順序で重ね合わせ、或いは、フロントカバー/変性オレフィン系樹脂シート/太陽電池素子/変性オレフィン系樹脂・バックカバー積層物シートをこの順序で重ね合わせ、変性オレフィン系樹脂の融点より高い温度、好ましくは融点より10℃以上高い温度で、通常1~60分程度、好ましくは5~30分程度の時間、通常20~200kPa程度、好ましくは30~150kPa程度の加圧下で、融着積層することによりなされる。

【0025】

【実施例】以下、本発明を実施例により更に具体的に説明するが、本発明はその要旨を越えない限り、以下の実施例に限定されるものではない。

【0026】実施例1

密度0.910g/cm³、190℃でのメルトフローレート3.5g/10分の直鎖状エチレン-1-オクテン共重合体100重量部、ビニルトリメトキシシラン2重量部、及びジクミルパーオキサイド0.06重量部を、2分間ドライブレンドした後、スクリー径40mm、L/D25の一軸押出機に供給し、220℃で熔融混練してグラフト反応工程に付した後、ストランド状に

溶融押出し、ペレット化することにより、ビニルトリメトキシシラン変性直鎖状エチレン-1-オクテン共重合体(次表中、「シラングラフトLLDPE」と表示。)のペレットを得た。得られた変性物は、ビニルトリメトキシシラン単位の含有量1.5重量%、190℃でのメルトフローレート2g/10分、融点112℃であり、又、未反応のジクミルパーオキサイドをメタノールで抽出し、ガスクロマトグラフを用いて分析した含有量は、0.001重量%以下であった。

【0027】このビニルトリメトキシシラン変性直鎖状エチレン-1-オクテン共重合体を、幅1000mmのTダイを備えた、スクリュ径65mm、L/D26の押出機より、ダイ温度150℃でシート状に溶融押出し、冷却することにより、厚み0.6mmの変性オレフィン系樹脂シートを成形した。このシート成形を5時間にわたって行ったが、その間の成形性は安定していた。又、以下に示す方法でゲル分率を測定し、結果を表1に示した。

ゲル分率

キシレン沸点にて10時間ソックスレー抽出した後の不溶分の重量%を測定した。

【0028】得られたシートを用いて、青板ガラス/変性オレフィン系樹脂シート/太陽電池素子/変性オレフィン系樹脂シート/ポリ弗化ビニルシート(米国デュポン社製「テドラー」)の順に重ね合わせ、58kPaの圧力下、表1に示す温度及び時間の条件で、融着積層した後、放冷することにより、太陽電池モジュールを製造し、得られた太陽電池モジュールについて、青板ガラスと変性オレフィン系樹脂シート間、及び、ポリ弗化ビニルシート(次表中、「PVF」と表示。)と変性オレフィン系樹脂シート間の各々について、接着状態を目視観察したところ、いずれも均一に接着していることが確認された。更に、以下に示す方法で剥離強度を測定し、又、剥離後の変性オレフィン系樹脂シートのゲル分率を前記と同じ方法で測定し、それぞれの結果を表1に示した。

剥離強度

10mm幅に切り取った試料を用い、引張速度100mm/分で90度剥離による剥離強度を測定した。

【0029】実施例2

酢酸ビニル単位含有量20重量%、190℃でのメルトフローレート15g/10分のエチレン-酢酸ビニル共重合体97重量部、酢酸ビニル単位含有量15重量%、190℃でのメルトフローレート2g/10分のエチレン-酢酸ビニル共重合体3重量部、ビニルトリメトキシシラン2重量部、及びメーブチルパーオキシ-2-エチルヘキサノエート0.3重量部を、2分間ドライブレンドした後、スクリュ径40mm、L/D25の一軸押出機に供給し、190℃で溶融混練してグラフト反応工程に付した後、ストランド状に溶融押出し、ペレット化

することにより、ビニルトリメトキシシラン変性エチレン-酢酸ビニル共重合体(次表中、「シラングラフトEVA」と表示。)のペレットを得た。得られた変性物は、ビニルトリメトキシシラン単位の含有量1.3重量%、190℃でのメルトフローレート9g/10分、融点89℃であり、又、未反応のメーブチルパーオキシ-2-エチルヘキサノエートをメタノールで抽出し、ガスクロマトグラフを用いて分析した含有量は、0.001重量%以下であった。

【0030】得られたビニルトリメトキシシラン変性エチレン-酢酸ビニル共重合体を用いた外は、実施例1と同様にして、変性オレフィン系樹脂シートを成形したところ、成形性は安定していた。又、シートにおけるゲル分率を測定し、結果を表1に示した。更に、融着積層することにより太陽電池モジュールを製造し、青板ガラスと変性オレフィン系樹脂シート間、及び、ポリ弗化ビニルシートと変性オレフィン系樹脂シート間の各々について、接着状態を目視観察したところ、いずれも均一に接着していることが確認された。又、剥離強度を測定し、更に、剥離後の変性オレフィン系樹脂シートのゲル分率を測定し、それぞれの結果を表1に示した。

【0031】実施例3

アクリル酸エチル単位含有量19重量%、190℃でのメルトフローレート5g/10分のエチレン-アクリル酸エチル共重合体100重量部、ビニルトリメトキシシラン2.5重量部、及びメーブチルパーオキシ-2-エチルヘキサノエート0.3重量部を、2分間ドライブレンドした後、スクリュ径40mm、L/D25の一軸押出機に供給し、190℃で溶融混練してグラフト反応工程に付した後、ストランド状に溶融押出し、ペレット化することにより、ビニルトリメトキシシラン変性エチレン-アクリル酸エチル共重合体(次表中、「シラングラフトEEA」と表示。)のペレットを得た。得られた変性物は、ビニルトリメトキシシラン単位の含有量1.4重量%、190℃でのメルトフローレート4.5g/10分、融点90℃であり、又、未反応のメーブチルパーオキシ-2-エチルヘキサノエートをメタノールで抽出し、ガスクロマトグラフを用いて分析した含有量は、0.001重量%以下であった。

【0032】得られたビニルトリメトキシシラン変性エチレン-アクリル酸エチル共重合体を用いた外は、実施例1と同様にして、変性オレフィン系樹脂シートを成形したところ、成形性は安定していた。又、シートにおけるゲル分率を測定し、結果を表1に示した。更に、融着積層することにより太陽電池モジュールを製造し、青板ガラスと変性オレフィン系樹脂シート間、及び、ポリ弗化ビニルシートと変性オレフィン系樹脂シート間の各々について、接着状態を目視観察したところ、いずれも均一に接着していることが確認された。又、剥離強度を測定し、更に、剥離後の変性オレフィン系樹脂シートのゲ

ル分率を測定し、それぞれの結果を表1に示した。

【0033】実施例4

内容積1.5リットルの攪拌機付き反応器にエチレン、 γ -メタクリロイルオキシプロピルトリメトキシシラン、及びアクリル酸メチルの混合物、並びにトブチルパーオキシネオデカノエートを連続的に供給し、重合圧力200MPa、重合温度190℃で共重合させることにより、エチレン- γ -メタクリロイルオキシプロピルトリメトキシシラン-アクリル酸メチル三元共重合体（次表中、「シラン共重合LDPE」と表示。）のペレットを得た。得られた変性物は、 γ -メタクリロイルオキシプロピルトリメトキシシラン単位の含有量1.1重量%、アクリル酸メチル単位の含有量25重量%、190℃でのメルトフローレート10g/10分、融点81℃であり、又、未反応のトブチルパーオキシネオデカノエートをメタノールで抽出し、ガスクロマトグラフを用いて分析した含有量は、0.001重量%以下であった。

【0034】得られたエチレン- γ -メタクリロイルオキシプロピルトリメトキシシラン-アクリル酸メチル共重合体を用いた外は、実施例1と同様にして、変性オレフィン系樹脂シートを成形したところ、成形性は安定していた。又、シートにおけるゲル分率を測定し、結果を表1に示した。更に、融着積層することにより太陽電池モジュールを製造し、青板ガラスと変性オレフィン系樹脂シート間、及び、ポリ弗化ビニルシートと変性オレフィン系樹脂シート間の各々について、接着状態を目視観察したところ、いずれも均一に接着していることが確認された。又、剥離強度を測定し、更に、剥離後の変性オレフィン系樹脂シートのゲル分率を測定し、それぞれの結果を表1に示した。

【0035】比較例1

実施例2で得られたビニルトリメトキシシラン変性エチレン-酢酸ビニル共重合体100重量部にジクミルパーオキサイド2重量部を添加して用いた外は、実施例1と同様にして、変性オレフィン系樹脂シートを成形したと

ころ、成形開始後15分で耳部に架橋反応が生起し、シート成形が困難となった。又、成形が良好のときのシートについてゲル分率を測定し、結果を表1に示した。更に、成形が良好のときのシートを用いて融着積層することにより太陽電池モジュールを製造し、青板ガラスと変性オレフィン系樹脂シート間、及び、ポリ弗化ビニルシートと変性オレフィン系樹脂シート間の各々について、接着状態を目視観察したところ、いずれもラジカル発生剤の分解生成物によるとみられる気泡が多く認められ、接着していない部分が多数存在していた。又、剥離強度を測定し、更に、剥離後の変性オレフィン系樹脂シートのゲル分率を測定し、それぞれの結果を表1に示した。

【0036】比較例2

アクリル酸エチル単位含有量19重量%、190℃でのメルトフローレート5g/10分、融点90℃のエチレン-アクリル酸エチル共重合体100重量部に、 γ -メタクリロイルオキシプロピルトリメトキシシラン1.5重量部、及びジ-トブチルパーオキサイド1重量部を添加して用いた外は、実施例1と同様にして、変性オレフィン系樹脂（次表中、「シラングラフトEEA」と表示。）シートを成形したところ、成形開始後20分で耳部に架橋反応が生起し、シート成形が困難となった。

又、成形が良好のときのシートについてゲル分率を測定し、結果を表1に示した。更に、成形が良好のときのシートを用いて融着積層することにより太陽電池モジュールを製造し、青板ガラスと変性オレフィン系樹脂シート間、及び、ポリ弗化ビニルシートと変性オレフィン系樹脂シート間の各々について、接着状態を目視観察したところ、いずれもラジカル発生剤の分解生成物によるとみられる気泡が多く認められ、接着していない部分が多数存在していた。又、剥離強度を測定し、更に、剥離後の変性オレフィン系樹脂シートのゲル分率を測定し、それぞれの結果を表1に示した。

【0037】

【表1】

表 1

	変性オレフィン系樹脂シート			積層条件		モジュール製造後の樹脂シート		
	樹脂種類	ラジカル発生 剤含有量 (重量%)	ゲル分率 (%)	温度 (℃)	時間 (分)	ゲル分率 (%)	接着強度(N/10mm)	
							対ガラス	対PVF
実施例 1	シラングラフト LLDPE	≤0.001	2	130 150	30 15	73 80	21 35	15 30
実施例 2	シラングラフト EVA	≤0.001	5	130 150	30 15	71 74	28 43	24 39
実施例 3	シラングラフト BBA	≤0.001	3	130 150	30 15	75 76	25 41	22 39
実施例 4	シラン 共重合LDPE	≤0.001	5	130 150	30 15	82 84	33 52	26 41
比較例 1	シラングラフト EVA	1.65	14	130 150	30 15	47 82	10 48	4 45
比較例 2	シラングラフト BBA	0.92	11	130 150	30 15	53 85	12 50	5 46

【0038】

【発明の効果】本発明によれば、フロントカバー或いは

バックカバーとの接着強度に優れる太陽電池モジュール
の製造方法を提供することができる。